AD-A254 818   N PAGE

1. AG		3. REPORT TYPE AND DATES COVERED
	June 12, 1992	Technical — 5/31/91 – 6/30/92

4. TITLE AND SUBTITLE "STUDIES OF PLASTICIZED POLYMER ELECTROLYTES CONTAINING MIXED Zn(II) AND Li(I)"

5. FUNDING NUMBERS

6. AUTHOR(S)

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G—N00014-90-J-1559

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

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DTIC
SELECTE
SEP.01 1992
B

8. PERFORMING ORGANIZATION REPORT NUMBER

1992-21

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

Sponsoring Agency:
DARPA
3701 N. Fairfax Drive
Arlington, VA 22203-1714

Monitoring Agency:
ONR
800 N. Quincy Street
Arlington, VA 22217-5000

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION/AVAILABILITY STATEMENT

Distribution Unlimited

DISTRIBUTION STATEMENT A
Approved for public release;
Distribution Unlimited

12b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)

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92   8 28 085

92-23983

14. SUBJECT TERMS

poly(ethylene glycol) (PEG), poly(ethylene glycol dimethyl ether) (PEGDME), electrolytes, zinc salt, lithium salt, amorphous regions, mixed-cation effect

15. NUMBER OF PAGES
9

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
Unclassified	Unclassified	Unclassified	UL

OFFICE OF NAVAL RESEARCH

GRANT NO.: N00014-90-J-1559

R & T CODE NO.: A400004DF3

TECHNICAL REPORT NO.: 1992-21

"STUDIES OF PLASTICIZED-POLYMER ELECTRILYTES
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by

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June 12, 1992

Studies of Plasticized-Polymer Electrolytes Containing Mixed Zn(II) and Li(I)

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Abstract

Thin solid films of mixtures of PEGDME and PEO containing various ratios of $ZnBr_2$ and LiBr have been prepared. Equal parts of PEGDME and PEO were used, and the ether oxygen to total metal ratio was kept constant at 16. TG data have shown that the thermal stability of the polymer electrolytes is affected moreso by the zinc salt than the lithium salt. DSC data show that these electrolytes are inhomogeneous mixtures of amorphous regions and crystalline PEO and PEO/salt complexes. Conductivity data did not show a mixed-cation effect.

1. Introduction

A variety of high conductivity polymeric electrolytes have been developed over the past 10-15 years. Most commonly, they consist of polymers such as polyethylene oxide (PEO) or polypropylene oxide (PPO) in which ionic salts are dissolved. Initial investigations were focused, for the most part, on lithium ion conducting electrolytes, but recent years have seen a growth of interest directed towards the synthesis and characterization of other ion conducting polymer electrolytes including those formed by dissolving salts of divalent and trivalent cations (1,2).

Several approaches have been taken to improve the conductivity of polymer electrolytes, including the addition of plasticizers, among them poly(ethylene glycol) (PEG) and poly(ethylene glycol dimethyl ether) (PEGDME). The addition of salts to either PEO or plasticized-PEO strongly influences the conducting properties, thermal stability, melting and glass transition temperatures of the electrolytes (3,4). Studies on glasses (5), beta/beta"- aluminas (6), and a polymer electrolyte of composition, $[0.5Ca(CF_3SO_3)_2 + 0.5Mg(CF_3SO_3)_2][PEO]_{15}$, (7) have shown that the presence of two different cations produces nonlinear deviations in such physical properties as conductivity, dielectric loss and internal friction. The maxima or minima usually observed in these data as a function of the mole fraction of cations have been referred to as the "mixed-cation effect".

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Recent studies on different compositions of $ZnBr_2[xPEGDME+(1-x)PEO]_n$, in which n is the mole ratio of ether oxygens to the metal ions, have shown that the specific composition with n=16 and x=0.5 has an exceptionally high conductivity and good mechanical properties (8). Furthermore, studies of $[xZnBr_2+(1-x)LiBr][PEO]_{16}$ have shown that the conductivity of the mixed-salt electrolytes is higher than that of either pure salt electrolyte (8). Similar studies on $[xMgBr_2+(1-x)LiBr][PEO]_{16}$ and $[xKSCN+(1-x)NaSCN][PPO]_{9.6}$ have shown no mixed-cation effect (8,9). In this paper we present the results of thermal and electrical characterization of solid polymer films of $[xZnBr_2+(1-x)LiBr][0.5PEGDME + 0.5PEO]_{16}$ with x ranging from 0.0 to 1.0.

2. Experimental Procedures

PEO (Aldrich, av. mol.wt.=5×10^6), PEGDME (Polyscience, av. mol.wt.=400), $ZnBr_2$ and LiBr (Aldrich, ultrapure) were used as starting materials. Acetonitrile (Aldrich) was added to PEO which had been dried for ~48 h at ~55°C under dynamic vacuum, and the mixture was stirred for 24 h to form a homogeneous solution. This solution was combined with PEGDME of the same weight as that of PEO and stirred for a further 6 h. To this resulting solution, stoichiometric amounts of $ZnBr_2$ and LiBr which had been earlier dissolved in anhydrous ethanol (Aldrich) were added and stirred for an additional ~18 h to ensure complete dissolution. The solution was then cast in a large glass ring on low-adhesion silicon paper and the solvent evaporated for ~48 h in an open atmosphere. The resulting films were heated at ~60°C for ~48 h under dynamic vacuum to remove residual solvent.

For bulk conductivity measurements, polymer samples of 10 mm diameter and approximately 0.25 mm thickness were placed between two spring loaded stainless steel electrodes. Complex ac impedance analysis was carried out using a Solartron 1250 Frequency Response Analyzer and 1286 Electrochemical Interface controlled by a Hewlett-Packard 9122 microcomputer. To ensure better contact between the electrodes and electrolyte and eliminate residual solvent, all samples except the one for which x=0.0 were first heated to 100°C in a flowing argon atmosphere and then allowed to cool to room temperature. The data reported here were obtained during a second heating cycle after the samples had remained at room temperature overnight under flowing argon.

A DuPont 910 differential scanning calorimeter (DSC) was used to determine the glass transition temperatures, melting temperatures, and other thermal

characteristics of the electrolytes. Hermetically sealed samples were used. Thermograms were recorded at a rate of $10°C/min$ under a nitrogen atmosphere. Each sample was first heated from $-120°C$ to $100°C$ and then allowed to cool to room temperature. Only those data obtained in a second heating cycle carried out from $-120°C$ to $250°C$ after a sample had remained overnight at room temperature are reported here. The thermal stability of the samples was studied by heating them in a nitrogen atmosphere at the rate of $10°C/min$ using a DuPont 951 Thermogravimetric Analyzer.

3. Results and Discussion

3.1 Thermal Studies

Thermogravimetric (TG) studies carried out on the films of various compositions have shown that they decompose in a complicated way. All the films exhibited a relatively small weight loss, <3% , in the temperature range 50 to $100°C$, presumably due to the evaporation of residual solvent or moisture absorbed when the samples were loaded. Above $100°C$, i.e after complete dehydration, no further weight loss was detected until irreversible decomposition began around $150°C$. A typical TG trace, e.g. for $x=0.4$ shown in Fig. 1 (curve a), exhibits the weight loss due to decomposition at three different temperatures, 273, 316 and $368°C$, with the maximum weight loss at $368°C$(seen clearly in Fig.1 curve b which is a derivative of heat flow with respect to time). Similar observations were made on all other samples with salt compositions in which the value of x ranged from 0 to 1.

In order to understand the origin of the various weight losses, TG experiments had also been carried out on pure PEGDME and PEO with PEGDME taken in equal ratio and the corresponding traces are given in Fig. 1 (curves c and d) for comparison. Curve c shows that the PEGDME begins to volatilize around $150°C$ with the maximum rate of loss being at $261°C$. Curve d shows that the weight loss in PEO with PEGDME taken in equal ratio begins around $200°C$ instead of $150°C$ and three distinct weight losses, two minor ones at 305 and $350°C$ and a major one at $412°C$. A comparison of all these data indicates that the first weight loss occurring at $261°C$ in PEGDME, or at $305°C$ in PEGDME- plasticized PEO, or at $273°C$ in PEGDME-plasticized PEO with salt present can be attributed to the loss of PEGDME. The weight loss occuring at about $412°C$ in PEGDME-plasticized PEO (curve d) appears to be due to the decomposition of PEO itself, as the pure PEO is known to decompose at

about 420°C. These results indicate that the thermal stability of PEGDME increases when mixed with PEO, but adding salt to the mixture decreases the thermal stability of the mixture somewhat, just as adding salt to PEO decreases the stability of PEO. Observation of an distinct weight loss which could be attributed to the loss of PEGDME in both PEGDME-plasticized PEO and PEGDME-plasticized PEO with salt suggests that at least a fraction of the PEGDME present in these samples is not as miscible in PEO as normally believed. The weight loss due to the volatilization of PEGDME and the final decomposition temperature (T_d) of PEO were found to depend on salt concentration. T_d varied from 385 to 335°C as the zinc content was increased from 0 to 100%. Thus the overall thermal stability of PEO is more affected by the concentration of the zinc salt than the lithium salt. The source of the decomposition occurring at 350°C in PEGDME-plasticized PEO or at 316°C in the x=0.4 composition is not clear.

Detailed DSC studies carried out in the temperature range of -120 to 250°C have shown that all the samples exhibited a glass transition (T_g) at around -45°C and an endothermic peak (T_m) at around 60°C that is attributable to the melting of crystalline PEO. The actual values of T_g and T_m varied with composition. Since the heat of melting for T_m is always less than 156 J/g, the value for crystalline PEO, it would appear that not all of the PEO present in the samples was crystalline. The DSC data for samples of all compositions that had been left at room temperature under vacuum for about 2 to 3 weeks are summarized in Table 1. In addition to T_g and T_m, all lithium-rich samples corresponding to x < 0.5 showed an intense broad endothermic peak (T_{m1}) at around 200°C and a small endothermic peak (T_{m2}) at around ±5°C. T_{m1} was noticeable even in those samples in which Zn content is not very high (x < 0.6). Since an endothermic peak at about 5°C had been observed in pure PEGDME also, T_{m2} could be attributed to the melting of immiscible PEGDME. The observation of T_{m2} in Li-rich samples alone imply that the effect of PEGDME as plasticizer may become less and less relevant as the concentration of Li-salt is progressively increased. T_{m1} can be attributed to the melting of crystalline PEO/salt complexes, the formation of which depend on the nature of metal ion, its bonding, and kinetics. The absence of T_{m1} in zinc-rich samples, particularly in those for for which x > 0.6, clearly shows that the complexation in these samples is relatively slow as compared to that in lithium-rich samples. Furthermore, in the first heating

Table 1: DSC data for $[xZnBr_2 + (1-x)LiBr][0.5PEGDME + 0.5PEO]_{16}$

x	T_g (°C)	T_{m2} (°C)	T_{m3}(°C)	T_m (°C)	T_{m1} (°C)
0.0	-44.0	4.6		63.1	197.8
0.2	-55.3	-7.9		61.6	182.8
0.4	-42.6	-5.7		64.3	208.5
0.5	-48.3		50.9	59.5	232.8
0.6	-44.0		46.0	58.4	191.8
0.8	-32.5		57.1	62.6	
1.0	-42.8		48.0	53.6	

cycle all the zinc-rich samples exhibited a small endothermic peak ($T_{m3} \sim 50°C$) close to that attributed to the melting of crystalline PEO. Since this peak disappeared after the first heating cycle, it may be attributed to the eutectic phase of PEO and PEO/salt complex. This might account for the absence of a high temperature T_{m1} in zinc-rich samples. It also suggests that the dissociation of $ZnBr_2$ may be less-complete compared to that of LiBr in PEGDME-plasticized PEO. All these data imply that the polymer electrolytes studied in the present investigation are inhomogeneous mixtures of amorphous regions, crystalline PEO, and PEO/salt complexes. Although T_g is expected to depend on the salt concentration in the amorphous phase, the presence of crystalline PEO/salt complex phase or eutectic phase of PEO and PEO/salt complex prevents us from making any correlation between the T_g values and salt concentration. Thus the absence of any systematic variation in T_g with salt concentration is not surprising.

3.2 Conductivity Studies

Fig. 2 shows plots of $\log(\sigma)$ vs. 1000/T for various electrolyte samples. The sample with x=0.0, i.e $LiBr[0.5PEGDME + 0.5PEO]_{16}$, has the highest conductivity (3.1×10^{-4} S/cm at 80°C) over the entire temperature range studied, 30 to 80°C, as compared to that (6.0×10^{-5} S/cm at 80°C) for x=1.0, i.e $ZnBr_2[0.5PEGDME + 0.5PEO]_{16}$. While conductivity values for the compositions 0.0<x<0.5 at temperature beyond the melting temperature of PEO are nearly same, for all other compositions the values lie between the above given limits. No mixed-cation effect is observed. The increase in conductivity observed for all the samples at ~60°C corresponds to the

melting of crystalline PEO. As was evident from DSC studies, Li-rich samples contain more of immiscible PEGDME and hence less of plasticizing effect. This fact may have great bearing on the lack of observation of mixed-cation effect. The sample for which x=0.0, i.e in which no zinc salt was present, exhibited a decrease in conductivity above $80^{\circ}C$, which may be due to an irreversible decomposition. For this very reason these samples were heated up to 80°C only in the first heating cycle. The addition of zinc salt appears to increase the electrolyte stability.

Reconsidering the DSC data for the composition range 0.7<x<1.0, the absence of a crystalline PEO/salt complex melting transition and the presence of eutectic phase of PEO and PEO/salt complex melting at $\sim 50^{\circ}C$ suggests that any temperature increase above $65^{\circ}C$ should release more salt into the amorphous conducting phase. Such a situation should create more effective charge carriers to contribute to the total conductivity if the $ZnBr_2$ is completely dissociated. However, the conductivity showed little change at $T\sim 65^{\circ}C$, which suggests that most of the $ZnBr_2$ exists as ion pairs and clusters.

Acknowledgements

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Figure Captions

Fig.1. Thermograms of different polymers. (a) for $[xZnBr_2 + (1-x)LiBr][0.5PEGDME + 0.5PEO]_{16}$ with x=0.4, (b) derivative of curve a with respect to time, (c) for PEGDME, and (d) for PEO+PEGDME taken in equal ratio.

Fig.2. Plots of $\log(\sigma)$ vs. 1000/T for various electrolyte samples in the $[xZnBr_2+(1-x)LiBr][0.5PEGDME + 0.5PEO]_{16}$ system with x ranging from 0.0 to 1.0.
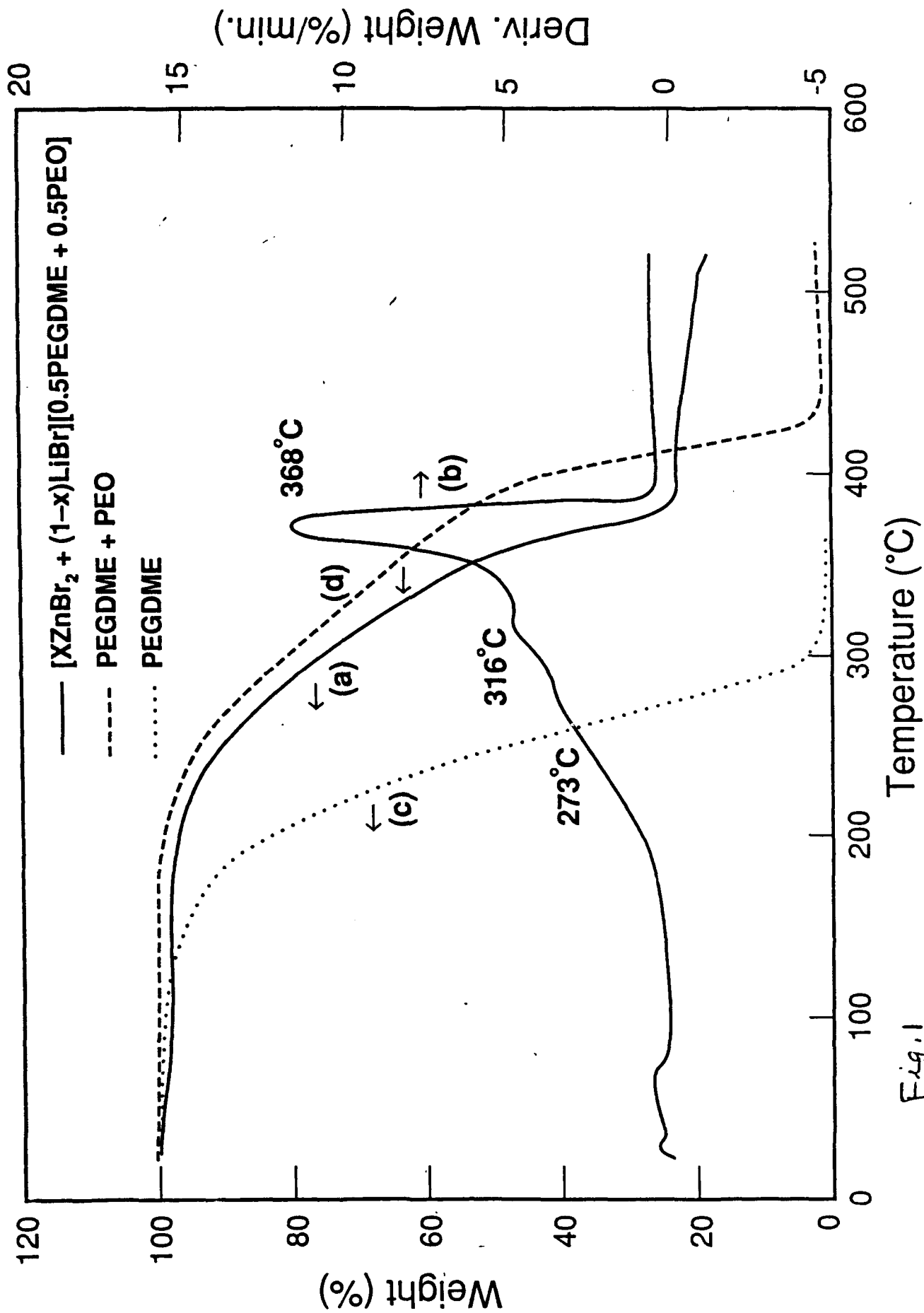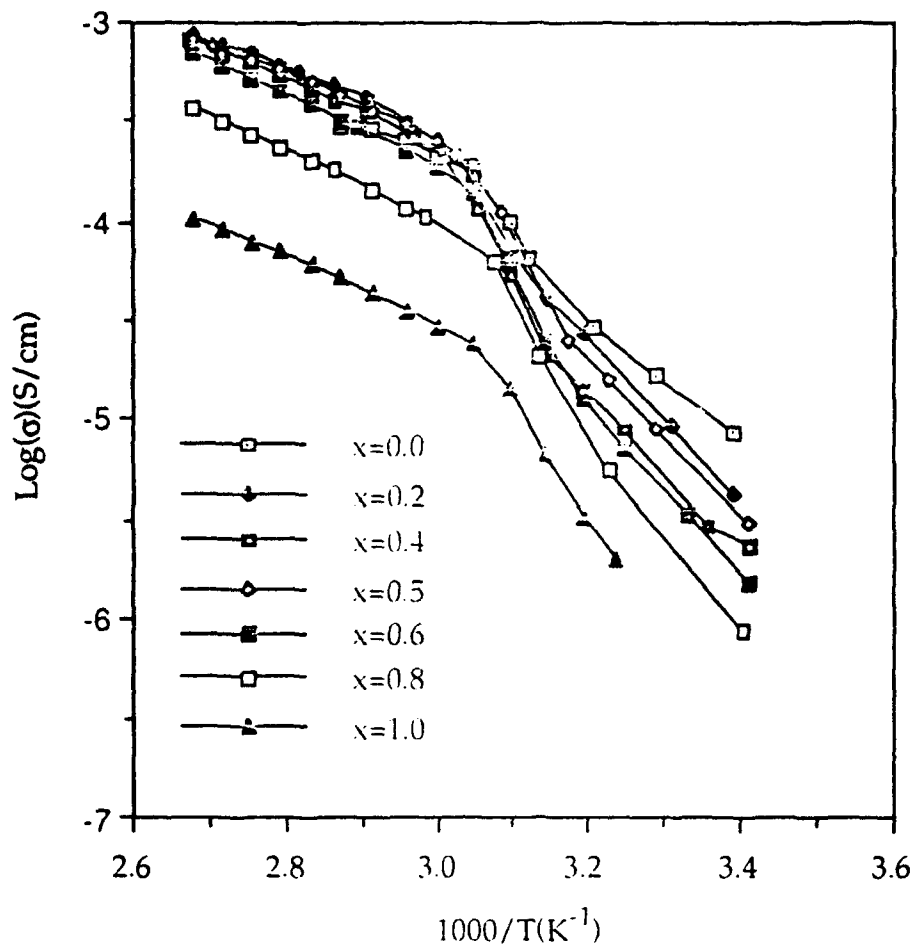
Fig. 1

Deriv. Weight (%/min.)

Weight (%)

Temperature (°C)

[XZnBr$_2$ + (1–x)LiBr][0.5PEGDME + 0.5PEO]

PEGDME + PEO

PEGDME

368°C

(b)

(d)

(a)

316°C

273°C

(c)

Figure axis labels:
- Y-axis: Log(σ)(S/cm), scale from -3 to -7
- X-axis: 1000/T(K^{-1}), scale from 2.6 to 3.6

Legend:
- x=0.0
- x=0.2
- x=0.4
- x=0.5
- x=0.6
- x=0.8
- x=1.0